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## Note: Achieving quasi-hydrostatic conditions in large-volume toroidal anvils for neutron scattering to pressures of up to 18 GPa

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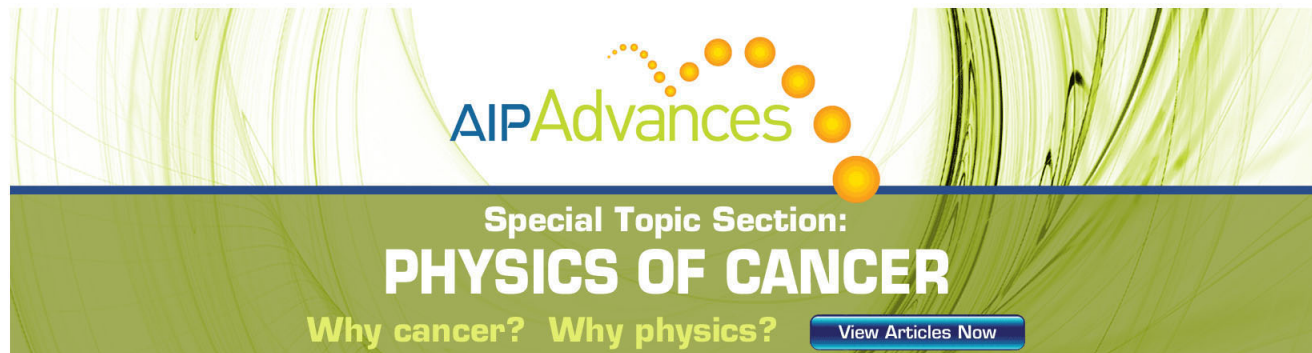
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## Note: Achieving quasi-hydrostatic conditions in large-volume toroidal anvils for neutron scattering to pressures of up to 18 GPa

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We present developments that allow neutron-scattering experiments to be performed, with both single-crystal and powder samples, under quasi-hydrostatic conditions to pressures beyond previous limits. Samples of sodium chloride and squaric acid ( $\text{H}_2\text{C}_4\text{O}_4$ ) have been loaded with argon as the pressure-transmitting medium in encapsulated gaskets redesigned for double-toroidal anvils, using a gas-loading method at ambient temperature. These samples have been compressed up to 18 GPa in a Paris-Edinburgh press, and no evidence of peak broadening in either the single-crystal or the powder experiments was observed. © 2011 American Institute of Physics. [doi:10.1063/1.3606643]

Until recently, the pressure achievable in a high-resolution single-crystal neutron-diffraction experiment has been limited by the available anvil and gasket technology. This has been a consequence primarily of the relatively large sample volume, of several cubic mm, required to perform such studies. More recently, we have developed new anvil and cell technologies that make such experiments possible to pressures of up to 12 GPa in quasi-hydrostatic conditions, using a Paris-Edinburgh press.<sup>1</sup> The maximum pressure of 12 GPa was set by the limit in hydrostaticity of the methanol:ethanol (4:1) pressure medium used.<sup>2</sup> It has been suggested by Fujishiro *et al.* that inclusion of one part of water in the solution (16:3:1) could increase the hydrostatic limit to 14 GPa,<sup>3</sup> but this has now been shown not to be the case.<sup>4</sup> (Inclusion of water could also be a problem in that some samples will dissolve in or react with it.) Recently, Klotz *et al.* described a method of increasing pressure while the methanol:ethanol medium is heated to about 100 °C, and showed that this could increase the limit of quasi-hydrostatic pressure to ~17 GPa.<sup>5</sup> However, some samples would be damaged or lost if taken to 100 °C at high pressure, and also compressing in steps that involve heating and cooling cycles can be time-consuming and difficult for large volume presses. An alternative would be to use an inert gas as a pressure medium.

Gases like argon or nitrogen can be loaded as cryogenic liquids, but some of the liquid boils off in this procedure and this can “wash out” part or all of a powder sample, and single-crystal samples can be damaged through the rapid cooling involved. The recent development of a gas-loading device for the Paris-Edinburgh (PE) press<sup>6</sup> now provides the better and simpler alternative of loading a gas medium at room temperature. In this note, we describe the developments that have allowed us to perform both single-crystal and powder neutron-diffraction studies up to ~18 GPa with argon as a quasi-hydrostatic medium, by using the gas-loader,<sup>6</sup> modified

double-toroidal sintered-diamond anvils,<sup>7</sup> and newly developed gaskets.

The recent work of Klotz *et al.* examines the hydrostaticity of various pressure-transmitting media currently used in high-pressure experiments.<sup>4</sup> The best pressure-transmitting medium for use beyond 10 GPa would be helium. However, even when loaded at ~200 MPa, the volume of the helium enclosed with the sample would have to be reduced by a factor of ~7 before the helium solidified, and no significant sample pressure would be generated prior to anvil or gasket failure – because the maximum reduction in the overall sample volume in a PE press is limited to a factor of ~3, and a large part of this would be used simply to solidify the helium. Furthermore, neutron absorption by helium can be a problem for performing neutron diffraction experiments. The better choice for use with the PE press is argon. It was shown by Klotz *et al.*<sup>4</sup> to provide quasi-hydrostatic conditions up to ~18 GPa; it has a compression ratio of only ~2 before solidification at 1.43 GPa when loaded at 130 MPa;<sup>8</sup> and its absorption of neutrons is not significant enough to reduce the quality of diffraction data.

A schematic of the sample and anvil assembly is shown in Fig. 1. A single crystal of sodium chloride was shaped to a cylinder with a volume of ~0.65 mm<sup>3</sup>. The sample was mounted in a modified version of the double-toroidal encapsulated gasket, in which a table provides a means to maintain alignment of the solid sample throughout the experiment.<sup>1,7,9</sup> The sodium chloride crystal was firmly attached to the flat surface of the table using cyanoacrylate adhesive. The gasket assembly was mounted in a pair of double toroidal sintered-diamond anvils<sup>7</sup> for which the fretage diameter had been slightly reduced to fit in the recently designed PE gas loader.<sup>6</sup> Argon was loaded into a clamp specially designed for use with a PE press at a pressure of 125 MPa by methods described previously.<sup>6</sup> The clamp can be closed at a sufficient load to avoid any loss of gas, and the loaded clamp is then transferred into a VX3 PE press<sup>10</sup> for compression up to higher pressures.

The clamp assembly in the VX3 PE press was attached to a closed-cycle refrigerator (CCR) mount<sup>1</sup> which held the

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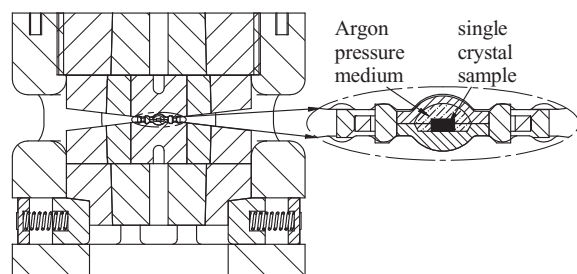


FIG. 1. A schematic of the double-toroidal anvils in the loading clamp with (shown enlarged) a single crystal attached to a gasket and surrounded by the argon medium. The gasket is shown in its initial uncompressed geometry.

press in position on the single-crystal instrument, SXD, at the ISIS Pulsed Neutron Source. Details of the instrument have been described elsewhere.<sup>1,11,12</sup> Since the current clamp was designed for the V4 variant of the PE press, and therefore has four apertures, while the VX3 variant of the PE press has two apertures,<sup>10</sup> the mutual orientation of the clamp and press was adjusted to maximise the common apertures, and align them with the position of the SXD detectors. Single-crystal reflection data from the sample were measured to establish the starting lattice parameters and peak position on the detectors, and obtain an orientation matrix. The load on the sample was then increased in 10-tonne steps and reflections were measured at each pressure point (i) to determine the relative change in reflection position in the time-of-flight (ToF) spectra and (ii) to observe any peak broadening that may occur as a result of non-hydrostaticity of the argon environment. For some pressure points, the diffraction data were collected for a longer time to increase the quality of the spectra and obtain a more precise determination of any changes in reflection widths.

The resolution of SXD is not high enough to determine pressure changes directly from derived lattice parameters. However, by following a single reflection, and its relative shift in ToF, it is possible to measure the pressure to within  $\sim 0.2$  GPa based on the NaCl equation of state (EoS) determined by Decker.<sup>13</sup>

In a separate experiment, a single crystal of squaric acid ( $\text{H}_2\text{C}_4\text{O}_4$ ),<sup>1,14</sup> with a volume of  $\sim 0.6 \text{ mm}^3$ , was loaded with an argon pressure medium, in the same way as described above for NaCl, and diffraction data were obtained at an applied load of 150 tonnes.

Experiments using the clamp and an argon-gas medium have also been performed on the PEARL/HiPr powder diffractometer at ISIS. Powder samples of both NaCl and  $\text{H}_2\text{C}_4\text{O}_4$  were loaded into standard encapsulated double-toroidal gaskets<sup>7,9</sup> with argon as a pressure medium, and diffraction patterns were obtained at loads up to 150 tonnes. The sample pressure was obtained directly from the determined lattice parameters for the powdered sample using the known EoS for each material.

The variation of pressure of the single crystal of NaCl with increasing load is shown in Fig. 2. After the initial compression of argon gas into its solid phase at 1.43 GPa, there is an approximately linear increase in pressure with increasing load up to  $\sim 125$  tonnes. The pressure achieved for a given load is significantly less than is obtained with a sample like

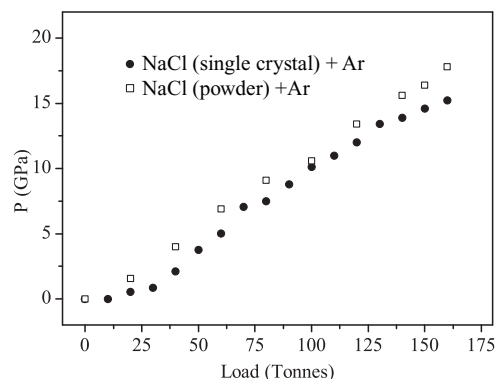


FIG. 2. Variation of sample pressure of NaCl with applied load for a single-crystal sample (filled circles) on the SXD instrument, and for a powder sample (open squares) on the PEARL/HiPr instrument.

water, for example, loaded in standard double-toroidal anvils and non-encapsulated TiZr gaskets,<sup>7</sup> but this is because of the large initial reduction of the sample volume required to compress the dense gas into a solid – estimated to be  $\sim 45\%$  in volume from the known equation of state of argon gas loaded at 130 MPa.<sup>8</sup> Figure 2 shows a decrease in the rate of increase in pressure with load above  $\sim 125$  tonnes, particularly for the single-crystal loading in this case, and experiments were stopped at an applied load of 160 tonnes to avoid anvil failure.

Figure 3(a) shows the spectrum in a single pixel of the SXD detector over the d-spacing range around the 200 single-crystal reflection of NaCl at 0.6, 1.0, and 15.2 GPa. The peak is seen shifting to lower d-spacing with increasing load, and the sample pressure was obtained from the d-spacing using the known EoS for NaCl as determined by Decker.<sup>13</sup> We observe no measurable change in the width of the reflection over the whole pressure range, and this indicates that good quasi-hydrostatic conditions are maintained. Figure 3(b) shows the 130 reflection from a single-crystal of  $\text{H}_2\text{C}_4\text{O}_4$  loaded in the same way and no change in peak width is observed at a pressure of  $\sim 15$  GPa. Also shown for comparison is the same reflection at  $\sim 1$  GPa.

Figure 2 also shows the pressure-load curve for a powdered sample of NaCl with argon as the pressure-transmitting medium, and the pressure performance is slightly better than for the single-crystal loading. This is most probably the result of there being a smaller volume of argon in the sample space for the powder sample, and the fact that argon is considerably more compressible than NaCl in this pressure range. A sample pressure of  $\sim 18$  GPa was ultimately achieved with this loading and no change in peak width was observed.

Powder diffraction patterns have also been obtained for  $\text{H}_2\text{C}_4\text{O}_4$  with argon as a pressure-transmitting medium. In Fig. 3(c), pattern A shows  $\text{H}_2\text{C}_4\text{O}_4$  at  $\sim 0.2$  GPa in its monoclinic phase, and pattern B shows the same sample at a load of 160 tonnes ( $\sim 14.5$  GPa) in its tetragonal phase. The peaks have moved to a lower d-spacing with the increased sample pressure and no visible change in peak width is observed.

In conclusion, we have shown that both powder and single-crystal neutron diffraction can be performed under quasi-hydrostatic conditions in a large-volume device to at

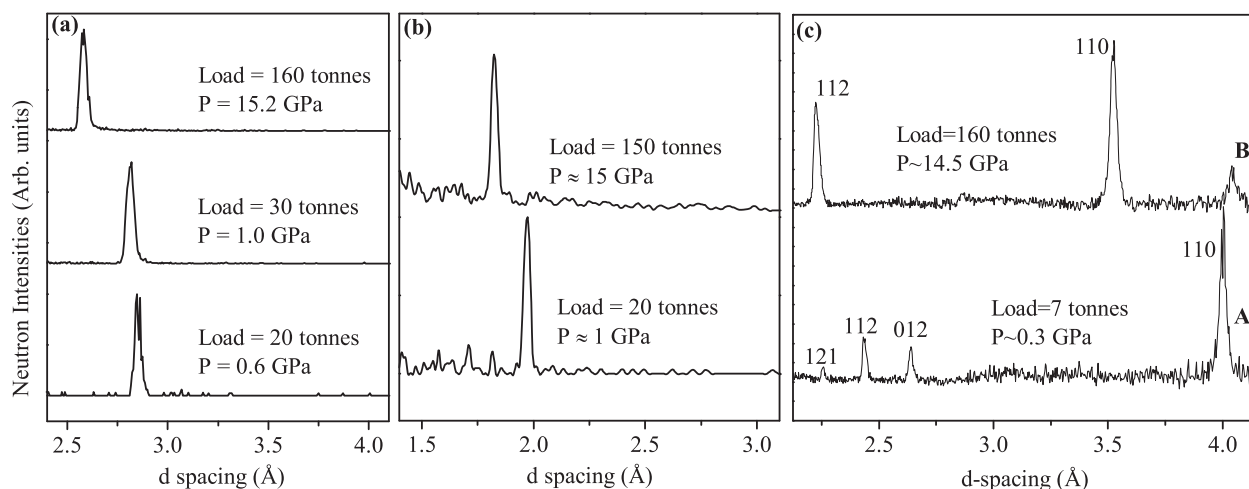


FIG. 3. (a) Showing the change in the spectrum for the 200 reflection of a single crystal of NaCl at three different applied loads. (b) The 130 reflection of H<sub>2</sub>C<sub>4</sub>O<sub>4</sub> at ~1 and 15 GPa. (c) Powder diffraction patterns of H<sub>2</sub>C<sub>4</sub>O<sub>4</sub>. Pattern A: squaric acid in the monoclinic phase, which exists up to 0.75 GPa (Ref. 14). Pattern B: the same sample at 160 tonnes and a pressure of ~14.5 GPa (in the tetragonal phase). The main reflections are indexed: the 012 reflection in A is non-allowed in the high-pressure tetragonal phase; the 121 reflection in A shifts out of the d-spacing range upon increasing pressure.

least the 15–20 GPa range, by using argon gas loaded at room temperature as the pressure-transmitting medium. This development will significantly increase the pressure range over which it is possible to carry out high-resolution neutron-diffraction studies. It may prove possible to increase the pressure range yet further by increasing the initial loading density of the gas, and work on this is in progress.

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